Improved productivity for the determination of metals in oil samples with ASTM Method D5185, using the Agilent 5100 Radial View (RV) ICP-OES

Application note

Petrochemical

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Introduction

The determination of metals in oils by ICP-OES using a radially-viewed plasma is a well established technique, especially for laboratories that implement ASTM Standard Test Method D5185-13. The method specifies ICP-OES for the rapid determination of 22 elements in used and unused lubricating oils and base oils, as well as rapid screening of used oils for wear-metals such as Fe, Cu and Al. Analysts use this test to monitor the condition of equipment for wear, to indicate the efficiency of the blending of additive packages, or for quality assurance of base oil for metal content.[1]

The Agilent 5100 Radial View (RV) ICP-OES takes the analysis to a new level of performance, particularly in terms of robustness, speed of analysis and reduced running costs. In this study, the 5100 RV was fitted with an Agilent SPS 3 Sample Preparation System and an Agilent SVS 2+ Switching Valve System which greatly improves productivity by reducing sample uptake, stabilization and washout times without compromising accuracy, precision, long-term stability and repeatability/reproducibility. With the faster sample run times, the 5100 RV requires less argon gas per sample, which can lead to significant savings for labs involved in high throughput analysis.

Agilent Technologies

Experimental

Instrumentation

The Agilent 5100 RV ICP-OES was used for this analysis. The dedicated radial view (RV) configuration is ideally suited to the analysis of organic samples. The plug-and-play torch mechanism automatically aligns the vertical torch and connects all gases for fast start up while ensuring reproducible loading of the torch, independent of the operator. Mass flow controllers on the three gas lines into the torch as well as thermostatted optics facilitate long term stability of the emission signal as seen in the long term stability plot in Figure 2.

To run challenging samples, the RF system must be able to rapidly adjust to changes in the plasma conditions. The free running solid state radio frequency (SSRF) generator in the 5100 RV ICP-OES meets these challenges and can handle a wide range of organic samples, from volatile organics such as methanol or gasoline, to semi volatile organics such as kerosene. The benefit of this is that plasma conditions similar to those used for aqueous solutions can be used for organics without the need for high plasma gas flows. An Agilent SPS 3 Sample Preparation System was used for automatic sample delivery in combination with the SVS 2+ Switching Valve System.

The sample introduction system chosen for this analysis was the semi-volatile organics kit comprising of a glass concentric nebulizer, a 1.4 mm id RV torch, solvent resistant tubing, and a double-pass glass cyclonic spray chamber.

Instrument operating conditions are listed in Tables 1a and 1b and the wavelengths selected for the analysis are given in Table 2. Wavelengths were selected according to the recommendations of ASTM D5185. Multiple wavelengths were selected for several elements to demonstrate the performance of the 5100 ICP-OES across the range of wavelengths that are typically used in the analysis. Method Detection Limits (MDLs) are also given in Table 2. They are based on three sigma of ten replicate measurements of the blank solution during the analytical run.

Fitted background correction was used for all wavelengths, simplifying the method development by eliminating the need to determine off-peak background correction points for each element.

Table 1a. Agilent 5100 RV ICP-OES and SVS 2+ Switching Valve System operating parameters

Parameter	Setting
Read time (s)	2
Replicates	3
Sample uptake delay (s)	0
Stabilization time (s)	10
Rinse time (s)	3 (fast pump: On)
Pump speed (rpm)	10
RF power (kW)	1.30
Aux flow (L/min)	1.0
Plasma flow (L/min)	12.0
Nebulizer flow (L/min)	0.65
SVS 2+ Switching Valve System operating parameters	
Loop uptake delay (s)	5
Uptake pump speed (Refill) (rpm)	350
Uptake pump speed (Inject) (rpm)	150
Sample loop size (mL)	0.5
Time in sample (s)	4
Bubble inject time (s)	4.8

Table 1b. Agilent 5100 RV ICP-OES method parameters

Parameters	Settings
Nebulizer	Glass concentric
Spray chamber	Double Pass Cyclonic
Torch	Organic 1.4 mm id
Sample tubes	White/white SolvaFlex
Drain tubes	Grey/grey SolventFlex
SPS 3 rinse solution	Kerosene
Background correction	Fitted

Table 2. Wavelengths used in the analysis. Method Detection Limits (MDLs) are also shown.

Element and line	MDL (mg/kg)	Element and line	MDL (mg/kg)	Element and line	MDL (mg/kg)
Ag 328.068	0.069	Fe 238.204	0.063	P 177.434	0.78
Al 308.215	0.065	Fe 259.940	0.085	P 178.222	4.6
Al 309.271	0.36	K 766.491	0.61	Pb 220.353	0.60
Al 396.152	0.12	Mg 279.553	0.068	Si 288.158	0.17
B 249.772	0.643	Mg 280.270	0.069	Si 251.611	0.43
Ba 233.527	0.042	Mg 285.213	0.066	Sn 189.925	1.92
Ba 493.408	0.064	Mn 293.305	0.058	Sn 242.170	1.55
Ba 455.403	0.058	Mn 257.610	0.063	Ti 334.941	0.074
Ca 317.933	0.35	Mo 202.032	0.065	Ti 337.280	0.069
Ca 422.673	0.40	Mo 203.846	0.20	Ti 350.490	0.21
Ca 315.887	0.38	Mo 281.615	0.092	V 292.401	0.070
Cd 226.502	0.054	Ni 221.648	0.45	V 309.310	0.049
Cr 205.560	0.12	Ni 231.604	0.23	V 310.229	0.077
Cr 267.716	0.065	Na 588.995	0.17	V 311.070	0.057
Cu 324.754	0.075	Na 589.592	0.29	Zn 202.548	0.16
Cu 327.395	0.060	P 213.618	0.62	Zn 213.857	0.18

Standard and sample preparation

Working standards of 0, 5, 10, 25 and 50 ppm were prepared from a Conostan S-21+K standard. This contains 22 elements (Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V and Zn) at 500 ppm in oil. These standards were matrix-matched for a constant viscosity using Conostan Element Blank Oil (75 cSt) and diluted with kerosene to give a total oil concentration of 10 % (w/w) in each solution.

Used engine oil samples were diluted 1:10 (w/w) with kerosene for the analysis. The samples were spiked with different concentrations of S21+K to test the recoveries of wear metal elements and additive elements. Low spike concentration was made at 25 ppm for all elements being determined. High concentration spikes, at 50 ppm for P and 100 ppm and 200 ppm for Zn and Ca were made. As with the standards, the samples were matrix-matched with the Element Blank Oil to give a total oil concentration of 10% (w/w) in each solution.

Results and discussion

Linear calibrations were obtained with correlation coefficient greater than 0.999 for all wavelengths. Figure 1 shows a calibration curve for Ca 422.673 up to 50 ppm with a correlation coefficient greater than 0.9999 and less than 1% calibration error on each calibration point. Because of the excellent linearity of the calibration curve, a 300 ppm in-solution spike could be accurately measured, highlighting the achieved linear dynamic range (LDR) of the 5100 RV ICP-OES. The expansive LDR also allows the number of calibration standards to be reduced, which means more time can be spent running samples, and less time will be spent on calibration.

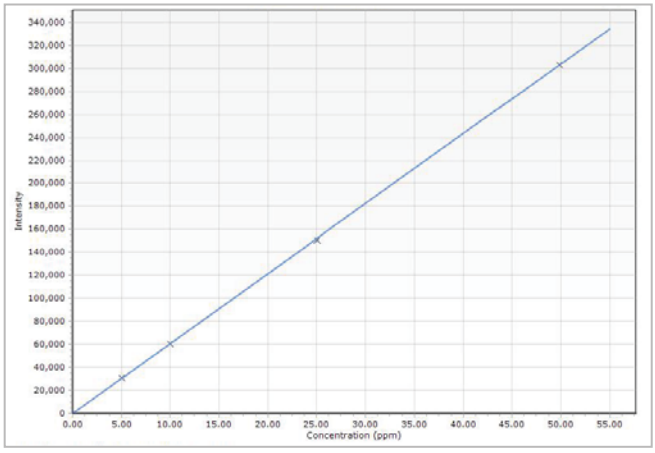

Figure 1. The calibration curve for Ca 422.673 nm up to 50 ppm shows excellent linearity across the calibrated range, with a correlation coefficient of 0.99998.

All elements were determined in the oil samples in a single run. The spike recoveries obtained with the 5100 RV ICP-OES are shown in Table 3. All values are within 10% of the expected values. Analysis time per sample was 30 seconds which includes a 3 second rinse between samples and a three replicate reading per sample. Total Ar consumption was only 9.5 L per sample.

Table 3. Agilent 5100 ICP-OES spike recoveries for all elements in used engine oil.
* <MDL = less than method detection limit

Element and line	Unspiked Sample (ppm)	Spiked Level (ppm)	Recovery (%)	Element and line	Unspiked Sample (ppm)	Spiked Level (ppm)	Recovery (%)	Element and line	Unspiked Sample (ppm)	Spiked Level (ppm)	Recovery (%)
Ag 328.068	<MDL*	25	96	Fe 238.204	0.45	25	98	P 177.434	39	50	96
Al 308.215	0.19	25	93	Fe 259.940	0.44	25	96	P 178.222	39	50	97
Al 309.271	0.13	25	95	K 766.491	0.019	25	92	Pb 220.353	0.015	25	101
Al 396.152	0.32	25	95	Mg 279.553	0.42	25	95	Si 288.158	0.30	24	95
B 249.772	5.43	25	103	Mg 280.270	0.41	25	98	Si 251.611	0.29	24	95
Ba 233.527	0.026	25	105	Mg 285.213	0.39	25	95	Sn 189.925	<MDL*	26	104
Ba 493.408	0.021	25	93	Mn 293.305	0.026	25	100	Sn 242.170	<MDL*	24	95
Ba 455.403	0.023	25	93	Mn 257.610	0.025	25	95	Ti 334.941	0.001	24	95
Ca 317.933	106	200	104	Mo 202.032	5.76	25	100	Ti 337.280	0.003	24	95
Ca 422.673	95	200	95	Mo 203.846	5.71	25	98	Ti 350.490	0.20	24	96
Ca 315.887	106	200	105	Mo 281.615	5.64	25	97	V 292.401	<MDL*	25	98
Cd 226.502	0.038	25	102	Ni 221.648	<MDL*	25	102	V 309.310	0.008	24	96
Cr 205.560	0.014	25	99	Ni 231.604	<MDL*	25	99	V 310.229	<MDL*	25	99
Cr 267.716	0.033	25	99	Na 588.995	1.24	25	92	V 311.070	<MDL*	24	97
Cu 324.754	0.130	25	93	Na 589.592	1.06	25	91	Zn 202.548	46.1	100	98
Cu 327.395	0.127	25	93	P 213.618	39	50	99	Zn 213.857	44.8	100	97

Long term stability of the 5100 RV ICP-OES was evaluated by setting up a complete analytical sequence with 3 seconds rinse time between each sample and measuring a 5 ppm S21 + K solution every 10 samples over a 4 hour period. Over the entire run 500 samples were analyzed without recalibration. The stability plot for all elements is displayed in Figure 2.

Stability ranged between 0.5 to 2.0 %RSD, with less than 4% deviation in concentration from the initial reading which demonstrates the robust sample handling capability of the vertically-oriented plasma in the 5100 RV ICP-OES, even when analyzing challenging organic samples.

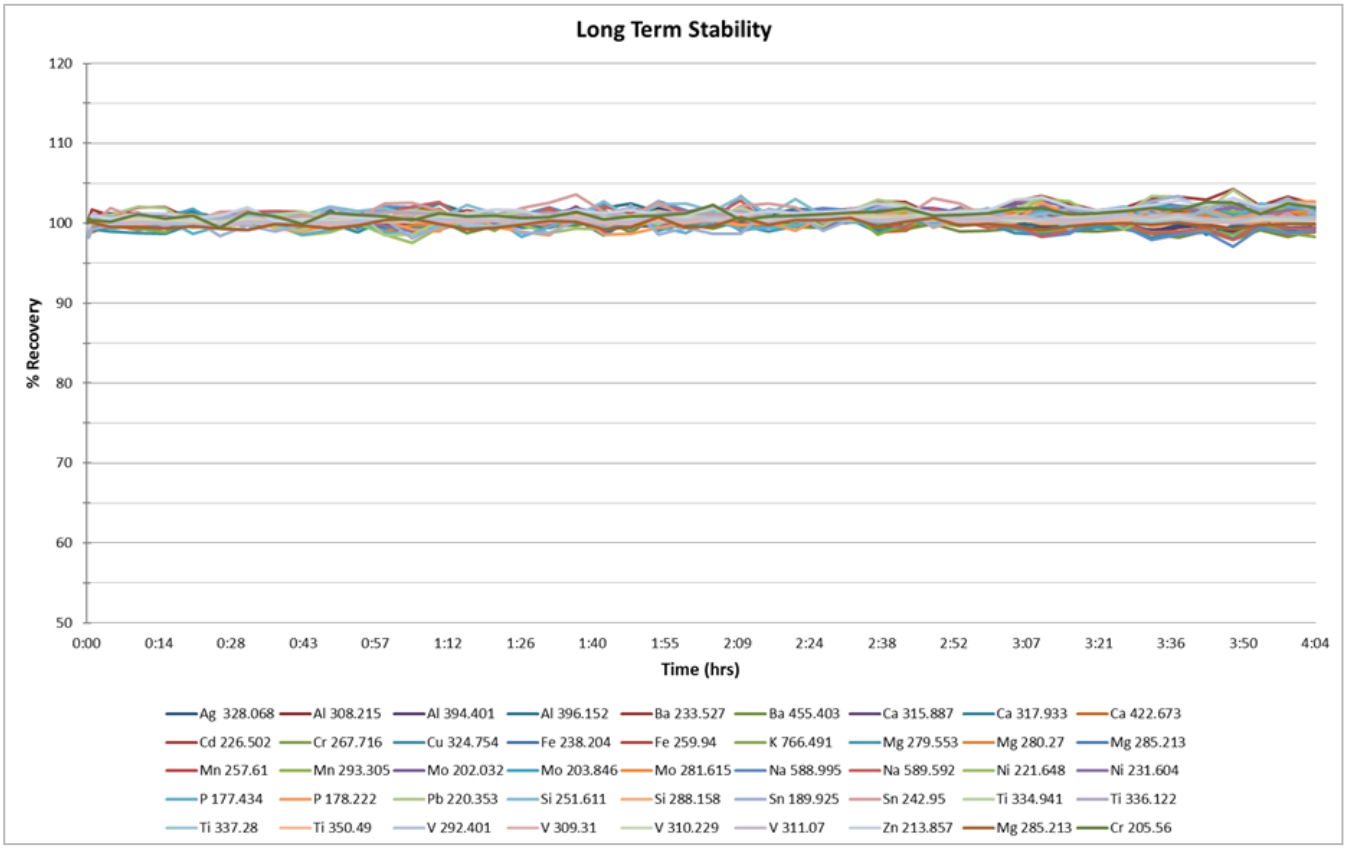

Figure 2. Stability plot over 4 hours for all elements in a used oil sample using the 5100 RV ICP-OES

Conclusions

The Agilent 5100 RV ICP-OES is the ideal instrument for determining metals in oil samples as per the ASTM D5185 method that is widely used by laboratories involved in the direct analysis of lubricating oils for wear metals and additives. The 5100 RV offers a number of advantages compared to other radial view ICP-OES:

- Sample analysis cycle time of 30 seconds per sample and total gas consumption of 9.5 L Ar per sample, using the SVS 2+ switching valve, without compromising accuracy, precision or stability
- Excellent long term stability with <2% RSD over 4 hours
- A vertical plasma and robust 27 MHz SSRF system delivers matrix handling capability and robustness
- Simplified day-to-day operation and method development due to an intuitive software interface
- Hardware features such as the plug-and-play torch lead to excellent method repeatability between operators and from instrument to instrument.

Reference

1. ASTM D5185-13, Standard Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

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